Stereochemical Nonrigidity in Some Poly(1-pyrazolyl)boratodicarbonylmolybdenum π-Allyls

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Abstract: The temperature dependence of the proton nmr spectra of some complexes of the form $RB(pz)_3Mo(CO)_2$-π-allyl has been studied (pz stands for 1-pyrazolyl and the π-allyl residue may be substituted). Fluxional behavior was observed and a complete line-shape analysis has been carried out using a first-order density matrix treatment. Since three different chemical shift separations are averaged by the same rate process, characteristic line-shape behavior can be followed over a wider temperature range (−20 to +50°) than is usual for studies of this type, leading to quite precise activation parameters. Conclusions from an earlier qualitative study of the spectral behavior of these complexes have been revised in light of the present quantitative study. The mechanism involves an internal rotation of the $RB(pz)_3^-$ group around the B–Mo axis, and to date $RB(pz)_3^-$ is the only tridentate ligand whose rotation around a transition metal can be conveniently studied by nmr.

In a recent publication[1] the stereochemical nonrigidity of some transition metal complexes containing tris(1-pyrazolyl)borate ligands was described and their temperature-dependent proton nmr spectra were qualitatively analyzed. In this paper we present a quantitative analysis of the temperature-dependent ^1H nmr line shapes for seven molybdenum pyrazolyl borates of the type $R_1B(pz)_3Mo(CO)_2$-π-$CH_2C(R_2)CH_2$ and revise some of the conclusions of the earlier work. The basic mechanism must involve a rotation of the tridentate ligand analogous to the trigonal or Bailar twist[2] proposed for six-coordinate species. On the basis of electron count regarding π-allyl as a uninegative bidentate ligand, the complexes would be classified as formally seven coordinate; to date the only well-established case of intramolecular rearrangement in truly six-coordinate compounds is that for complexes of the form H_2ML_4 (M = Fe, Ru; L = phosphine or phosphite).[3] For these species the proposed rearrangement mechanism is not even formally analogous to the one considered here. The closest analogy to the present case would be the type of behavior to be expected in the corresponding half-sandwich complexes involving the π-C_5H_5 ligand. However, the activation energy for twisting in these systems appears to be so low that slow exchange limit nmr spectra cannot be obtained within the experimentally accessible temperature range.

Experimental Section and Calculations

The preparation of complexes of the type studied here has been described in the literature.[1,4]

Nmr samples were prepared using $CDCl_3$ as solvent and ^1H nmr spectra were recorded on Bruker HFX 90, Varian HR-220, and Varian HA-100 spectrometers. Detailed line-shape analysis for all seven complexes was carried out only for the spectra recorded on the Bruker HFX-90. For this instrument temperatures were measured with a copper–constantan thermocouple located just beneath the sample tube in the probe and were calibrated using a similar thermocouple held coaxially in a spinning nmr tube containing solvent. Temperature measurements are thought to be accurate to ±2°.

Although the exchange process is of the mutual exchange type, the temperature-dependent nmr spectra are most conveniently analyzed as an intramolecular exchange between two sites with populations in the ratio 2:1 (*vide infra*). The spectra are essentially first order and therefore the density matrix equations of Kaplan[5] and Alexander[6] simplify to the equations given by Sack[7] and the calculation of nmr line shapes using the former approach becomes quite straightforward. A general computer program has been written for the case of intramolecular exchange of first-order spectra between several sites. This program employs the complex matrix diagonalization technique first introduced by Gordon and McGinnis[8] to avoid matrix inversion at each of the points needed to construct a Calcomp plot of the spectrum.

Results

The observed and calculated ^1H nmr spectra associated with the pyrazolyl groups for $pzB(pz)_3Mo(CO)_2$-π-CH_2CBrCH_2 are shown in Figure 1 at several temperatures and associated exchange rates. The transitions assigned to the 2-bromo-π-allyl protons were also recorded, but, since the spectra in this region are essentially temperature independent for all seven complexes at all temperatures attainable in the $CDCl_3$ solvent, they are not shown and will not be discussed further. The spectra shown in Figure 1 are typical for those complexes with a terminal pyrazolyl group. The complexes are believed to have one of the two structures A or B shown in Figure 2. Regardless of which conformation is correct, one of the bridging pyrazolyl groups will be unique and the other two identical (a similar conclusion applies to the nmr experiment if the π-allyl group is rotating rapidly on an nmr time scale; the observation of only two carbonyl stretching vibrations in the infrared, however, tends to suggest a rigid structure A or B).

The low-temperature limiting spectrum in Figure 1 is assigned as follows: doublets X and Y to the 3 and 5 protons, respectively, of the unique bridging pyrazolyl, doublets X′ and Y′ to the 3 and 5 protons, respectively, of the two identical bridging pyrazolyls, triplets Z and Z′ to the 4 protons of the unique and bridging pyrazolyls. The remaining resonances A

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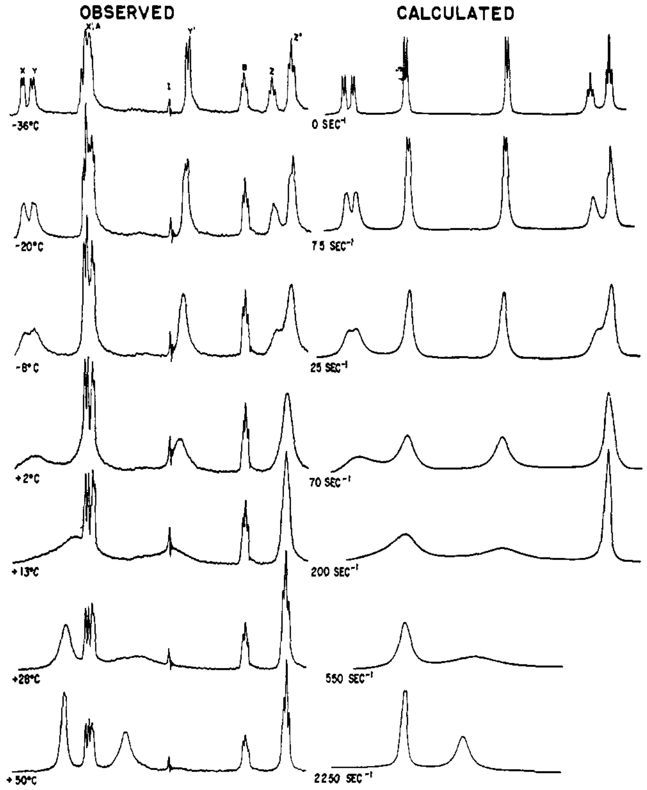

Figure 1. Observed and calculated 90-MHz ^{1}H nmr spectra for $pzB(pz)_3Mo(CO)_2$-π-CH_2CBrCH_2 at a series of temperatures (exchange rates). Using the numbering in Figure 2, X and X′ arise from the 3 protons of the bridging pyrazolyl groups in the slow exchange limit, Y and Y′ from the 5 protons, and Z and Z′ from the 4 protons. A corresponds to the 3,5 and B to the 4 protons of the terminal pyrazolyl group, and I is an impurity resonance ($CHCl_3$).

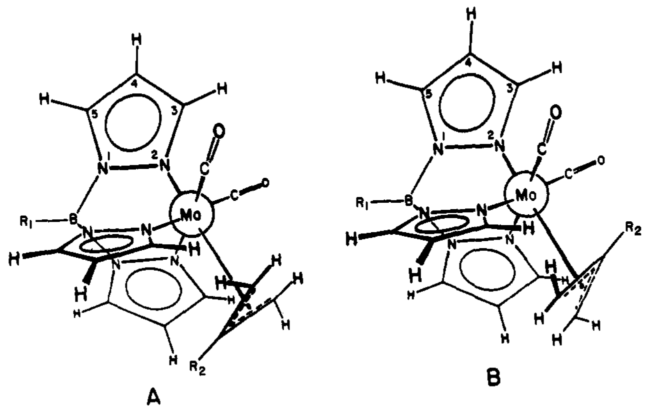

Figure 2. Numbering of ring positions and possible conformations for $R_1B(pz)_3Mo$-π-$CH_2C(R_2)CH_2$.

and B are assigned to the 3,5 and 4 protons of the terminal pyrazolyl. These resonances are unaffected by the exchange process and their nmr line shapes are essentially temperature independent. I indicates an impurity resonance ($CHCl_3$). In all seven cases $J_{34} \sim J_{45} \sim 2.2$ Hz for all three types of pyrazolyl and in some cases the splitting due to J_{35} can be resolved in the high-temperature limit and has a value of about 0.7 Hz. The nmr spectra for those complexes with a terminal proton have a somewhat different appearance and a typical example is shown in Figure 3 for $HB(pz)_3Mo(CO)_2$-π-$CH_2C(CH_3)CH_2$. In this figure the observed and calculated spectra of the resonances attributed to the 3 and 5 protons only are shown; X, X′ correspond to the 3 position and Y, Y′ to the 5 position.

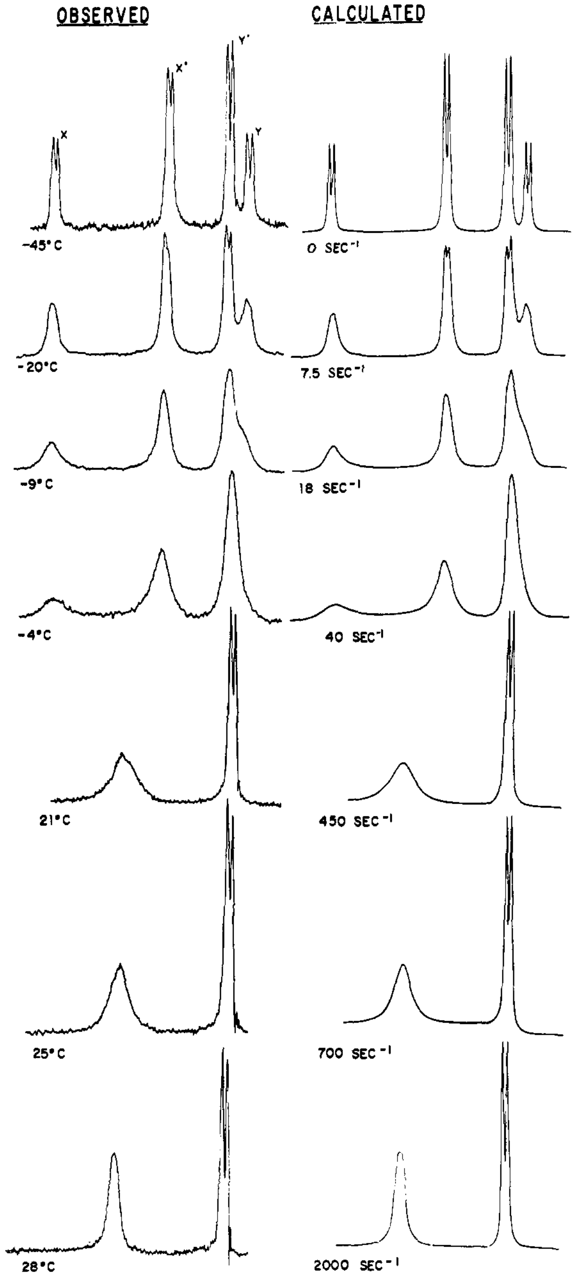

Figure 3. Observed and calculated 90-MHz ^{1}H nmr spectra for the 3- and 5-bridging pyrazolyl protons in $HB(pz)_3M(CO)_2$-π-$CH_2C(CH_3)CH_2$ at several temperatures (exchange rates). Using the numbering in Figure 2, X and X′ arise from the 3 position, Y and Y′ from the 5 position.

In those cases where the terminal substituent R_1 = H (Figure 2), the temperature dependence of the chemical shifts of all the lines in the pyrazolyl region is quite small (less than 4×10^{-4} ppm deg^{-1} in all cases); by contrast in those cases where X = pyrazolyl, the temperature dependence of the chemical shifts is larger particularly for the doublet Y′ ($\sim 20 \times 10^{-4}$ ppm deg^{-1}). We interpret this observation as follows. Because of hindered internal rotation about the B–N bond to the terminal pyrazolyl group there will be several conformations corresponding to each of the basic structures shown in Figure 2. If the barrier to internal rotation about the B–N bond is less than about 7–8 kcal, the internal rotation process will be rapid on the nmr time scale and the spectra for all of the internal rotation isomers will be averaged. Thus the chemical shifts observed will be given by

$$\delta_{\text{obsd}} = \sum_i p_i\delta_i \text{ with } \sum p_i = 1 \qquad (1)$$

where p_i is the population of the ith internal rotation isomer and δ_i is the corresponding chemical shift. If the energy separation between the internal rotation isomers is of the order of a few hundred calories, then the populations p_i will be appreciably temperature dependent over the temperature range for which the experiments were carried out. The fact that the chemical shifts of the 5 protons, which are closest to the terminal pyrazolyl, are the most temperature dependent supports this rationalization. In order to calculate accurate exchange rates the chemical shift separation must be known at all temperatures. Although we do not expect a linear temperature dependence of chemical shifts from the model described above, the range of temperatures over which the slow exchange limit spectra can be observed is too small (−60 to −10°) to justify any other type of extrapolation. The procedure is expected to be quite satisfactory provided it is not applied over too wide a temperature range and the good agreement obtained between calculated and observed spectra for all of the lines XX′, YY′, and ZZ′ (Figures 1 and 2) supports the use of this approach. If the extrapolation is not made and the chemical shifts are held at their low-temperature limit values, the agreement between observed and calculated spectra is poor at the higher temperatures.

The assignment of the pyrazolyl proton absorptions to specific protons or pairs of protons is discussed in an earlier paper.[1] The association of the lines X and X′ with one ring position and of Y and Y′ with another is confirmed by the double resonance + exchange technique of Fung.[9] Thus, if the doublet X′ is strongly irradiated at a temperature such that the exchange rate is a few reciprocal seconds, the line X disappears due to transferral of saturation between X and X′. This shows that the protons associated with the X and X′ doublets are switched by the exchange process. Similarly, if the doublet Y′ is strongly irradiated, the doublet Y is saturated.

In all seven cases we find that within experimental error the doublets X and X′, the doublets Y and Y′, and the triplets Z and Z′ exchange at the same rate (see Figure 1). This fact together with the observation that the terminal and bridging pyrazolyls are not exchanged suggests that the process observed is a trigonal twist about the Mo–B axis. In Figure 4 the temperature dependence of the exchange rates for pzB(pz)$_3$Mo(CO)$_2$-π-CH$_2$CBrCH$_2$, determined from a visual fitting of the nmr line shapes, is shown as an Arrhenius plot. The straight line is given by $R(T) = 10^{12.09}\cdot e^{-12{,}800/RT}$ where $R(T)$ is the rate of exchange at temperature T, or in terms of the Eyring equation $R(t) = K(kt/h)e^{-\Delta G^{\ddagger}/RT}$ we find (assuming the transmission factor K to be 1)

$$\Delta G^{\ddagger}\ (298°) = 13.8 \text{ kcal mol}^{-1}$$

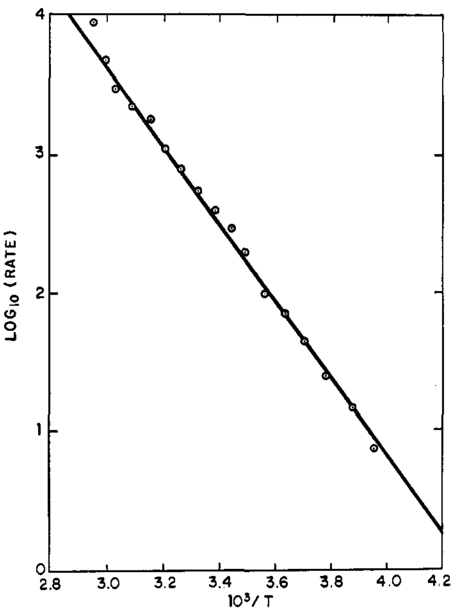

Figure 4. Arrhenius plot for the exchange process in pzB(pz)$_3$-Mo(CO)$_2$-π-CH$_2$CBrCH$_2$.

$$\Delta H^{\ddagger}\ (298°) = 12.2 \text{ kcal mol}^{-1}$$

$$\Delta S^{\ddagger}\ (298°) = -5.2 \text{ cal mol}^{-1} \text{ deg}^{-1}$$

The results for all seven complexes are shown in Table I.

Table I. Activation Parameters

Compound R$_1$	R$_2$	Log A	E, kcal mol^{-1}	$\Delta G^{\ddagger}$, kcal mol^{-1} (298°)	$\Delta H^{\ddagger}$, kcal mol^{-1} (298°)	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1} (298°)
H	H	12.3	14.2	14.8	13.6	−4.1
H	CH$_3$	13.4	14.5	13.6	13.8	1.0
H	C$_6$H$_5$	12.8	14.2	14.2	13.6	−2.0
Pz	H	13.5	15.7	14.8	15.1	1.0
Pz	Br	12.1	12.8	13.8	12.2	−5.2
Pz	CH$_3$	13.3	14.4	13.7	13.8	0.3
Pz	C$_6$H$_5$	11.7	12.9	14.4	12.2	−7.1

Since the exchange process averages three different chemical shift separations, exchange rates can be measured accurately over a large range of temperatures (−20 to +50°) and the activation parameters given in Table I should be quite accurate. However, the activation parameters are so similar for all seven complexes that only the differences in the $\Delta G^{\ddagger}$ values are significant. The results in Table I indicate that $\Delta G^{\ddagger}$ is insensitive to substitution of the terminal hydrogen by pyrazolyl but that there are significant differences for different substituents at the 2 position of the π-allyl moiety. The order of $\Delta G^{\ddagger}$ values for these substituents in H > C$_6$H$_5$ > CH$_3$.

As is expected for a simple intramolecular process such as a twist about the B–Mo axis, the entropies of activation are quite small. For a class of similar compounds such as the seven pyrazolyl borates studied here the entropies of activation should be quite similar and most of the observed spread is probably due to experimental and calculational error. The largest

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(9) B. M. Fung, *J. Chem. Phys.*, **49**, 2973 (1968); *J. Amer. Chem. Soc.*, **90**, 219 (1968).

source of error is probably in the temperature measurement; an error of ±2° could result in an error of as much as 3.5 cal mol^{-1} deg^{-1} in $\Delta S^{\ddagger}$, ±1 kcal mol^{-1} in $\Delta H^{\ddagger}$.

Discussion

In the original nmr work on complexes of the type $pzB(pz)_3Mo(CO)_2$-π-$CH_2C(R_2)CH_2$ the two environments of the 5 H protons were believed to be averaged less rapidly than the environments of the 3 H protons because a higher temperature was required to coalesce the 5 H resonances. This analysis failed to take into account the larger chemical shift difference between the 5 H doublets (Y,Y′) than that between the 3 H doublets (X,X′) (Figure 1). This apparent rate difference was explained in terms of hindered internal rotation of the terminal pyrazolyl group about the B–N bond and it was concluded that the barrier to internal rotation about the B–N bond was higher than that for the rotation of the three bridging pyrazolyls about the B–Mo axis. We now conclude that the rotation of the terminal pyrazolyl group is rapid on the nmr time scale at all temperatures attainable in $CDCl_3$ solution. Examination of a molecular model for complexes of the type $pzB(pz)_3Mo(CO)_2$-π-$CH_2C(R_2)CH_2$ based on the recently published[10] X-ray crystal structure for $HB(pz)_3Mo(CO)_2NNC_6H_5$ indicates that, during the internal rotation of the terminal pyrazolyl about the B–N bond, the nucleus of the 5 hydrogen of the terminal pyrazolyl and the nuclei of the 5 hydrogens of the bridging pyrazolyls approach to within about 1 Å of each other in the eclipsed conformation. The nonbonded H–H repulsion energy at such a short internuclear separation should be very large[11] and on this basis the barrier to internal rotation for the terminal pyrazolyl should also be very large. This result is clearly not in agreement with our interpretation of the temperature-dependent nmr spectra.

Apart from errors in the structural model we have used, the main source of this discrepancy may be due to the possibility that the terminal pyrazolyl bends toward the space between two of the bridging pyrazolyls as it eclipses the third and/or that the terminal B–N bond may stretch at the conformation where the 5 hydrogens of the terminal and bridging pyrazolyls are eclipsed, thus increasing the H–H internuclear separation. In this context we note that the three bridging pyrazolyls in $pzB(pz)_3Mn(CO)_3$ are equivalent on the nmr time scale at −30° indicating rapid internal rotation of the terminal pyrazolyl at this temperature[1] and similarly that the internal rotation of the terminal pyrazolyl group in $pzB(pz)_3Mo(CO)_3^-$ is fast, on the nmr time scale, at room temperature.[1] Our observation of high temperature limit spectra in which the three bridging pyrazolyls are equivalent on the nmr time scale requires that the internal rotation of the terminal pyrazolyl is rapid at these temperatures irrespective of the detailed interpretation of the temperature-dependent spectra. The possibility that the terminal pyrazolyl group is freely rotating in the high-temperature limit and in a fixed conformation with respect to the nmr experiment in the low-temperature limit seems unlikely in view of the fact that there are no line-shape effects for the absorptions associated with the terminal grouping.

The relatively large chemical shift separation of the 5 H doublets for those complexes containing a terminal pz as compared to those containing a terminal proton is still attributed to the influence of the fourth pyrazolyl. Despite the fact that the internal rotation is fast on the nmr time scale, the terminal pyrazolyl spends more time in the lower energy internal rotation conformations and consequently its time-averaged orientation is not isotropic. It therefore has a different average orientation with respect to the 5 H protons Y than it does with respect to the Y′ protons. The qualitative variation of the barrier with variation in molecular structure was also considered in the earlier publication.[1] It was found that spectra from corresponding molybdenum and tungsten complexes were essentially superimposable, consistent with the near identity of their atomic radii. Substitution at the 4 position on the pyrazolyl rings also had little effect on the barrier. The earlier qualitative conclusion that substituents in the 2 position of the allyl group such as CH_3 and C_6H_5 lead to *lower* barriers than for the parent complex is substantiated quantitatively by the present studies. There is a decrease in $\Delta G^{\ddagger}$ of ~0.6 kcal mol^{-1} on going from H to C_6H_5 and a similar decrease from C_6H_5 to CH_3 (Table I). It is clear from the ranking that, for a single basic configuration, the effect cannot be entirely steric in origin. The value for a bromo substituent lies very close to that for methyl. It is possible that the 2-H compound adopts configuration B and the 2-CH_3 and 2-C_6H_5 compounds adopt configuration A. With this assumption the ordering of the $\Delta G^{\ddagger}$ values can be rationalized on steric grounds. Substitution by methyls in the 3 position of the bridging pyrazolyl groups gives, as might be expected from the increased steric crowding, a substantially increased barrier to rotation.

In considering the actual physical process giving rise to the nmr line-shape effects, we can eliminate a mechanism which involves dissociation of one of the pyrazolyl bridges since the fourth pyrazolyl group maintains its identity in complexes involving the $B(pz)_4^-$ ligand. A dissociative mechanism of this type does appear to apply for complexes such as $Zn[B(pz)_4]_2$ where all four (pz) groups are equivalent on an nmr time scale.

The only realistic remaining possibilities are a trigonal twist of the $RB(pz)_3^-$ group around the B–Mo axis or a process involving carbon monoxide dissociation. We discard the latter alternative since there is no evidence for CO dissociation; the complexes can for instance be purified by sublimation and $pzB(pz)_3Mo(CO)_2$-π-allyl melts without decomposition at 253°.[4]

The tris(1-pyrazolyl)borate–molybdenum complexes which are the subject of our work are similar to the cyclopentadienylmolybdenum complexes of the type π-$C_5H_5Mo(CO)_2LR$ described by Faller and Anderson[12] [L = $P(C_6H_5)_3$, $P(n\text{-}C_4H_9)_3$, $P(CH_3)_2C_6H_5$, $P(OCH_3)_3$, $P(OC_6H_5)_3$; R = H, D, CH_3, $C_6H_5CH_2$, CH_3OCH_2, CH_3SCH_2, Cl, Br, I]. The π-C_5H_5 ligand is similar to the tris(1-pyrazolyl)borate ligand[4] and (L + R) corresponds to the $CH_2C(R_2)CH_2^-$ ligand.

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Two significant differences between these similar classes of compounds are (a) the barrier to internal rotation for the π-C_5H_5 group is low whereas the barrier to internal rotation for the tris(1-pyrazolyl)borate ligand about the Mo–B axis is quite high (see above); (b) in the case of the π-$C_5H_5Mo(CO)_2LR$ two isomers can be observed corresponding to cis and trans positions for the ligands L and R. In the present case the π-$CH_2C(R_2)CH_2^-$ ligand can occupy only two cis positions. The cis and trans isomers of the complexes π-$C_5H_5Mo(CO)_2LR$ can interconvert through an intramolecular process with a trans → cis barrier which varies between 12 and 26 kcal/mol^{-1} depending mainly on the nature of the ligand R.

Faller and Anderson[12] discuss this rearrangement process in terms of a pseudo-five-coordinate model for the complexes. The lowest energy configuration is considered to be approximately square pyramidal with the π-C_5H_5 ligand located at the apex and the four other ligands located at the base. The cis and trans isomers can then interconvert *via* a "trigonal-bipyramidal" intermediate with the π-C_5H_5 ligand in an axial position.

In the case of the tris(1-pyrazolyl)borate–molybdenum complexes, a process of the type described by Faller and Anderson[12] can exchange the two CO ligands or can exchange the two ends of the π-$CH_2C(R_2)CH_2^-$ ligand. However, the three bridging pyrazolyl groups cannot become equivalent on the nmr time scale unless internal rotation about the Mo–B axis occurs at some stage. It is quite possible that a combination of the two processes is taking place.

Olefin Coordination Compounds of Rhodium. VI. Dissociative Displacement of Ethylene from Rhodium(I) and the Strength of the Rh–C_2H_4 Bond in π-$C_5H_5Rh(C_2H_4)_2$

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Abstract: Ethylene can be cleanly displaced from π-$C_5H_5Rh(C_2H_4)_2$ by various nucleophiles through a mechanism whose rate-determining step is dissociative loss of C_2H_4. A study of the gas-phase pyrolysis of π-$C_5H_5Rh(C_2H_4)_2$ indicates a maximum value of about 31 kcal for the strength of the Rh–C_2H_4 bond in that compound.

Displacement of ethylene from acac$Rh(C_2H_4)_2$ by nucleophiles (CO, CN^-, phosphines, amines, etc.) is a very fast reaction. For example, the exchange rate of coordinated ethylene is $>10^4$ sec^{-1} at 25°.[1] This exchange occurs through the familiar bimolecular substitution mechanism of d^8 square-planar molecules;[2] ethylene is the attacking nucleophile. On the other hand, ethylene in π-$C_5H_5Rh(C_2H_4)_2$ is not easily displaced by nucleophiles[1,3] and this behavior is consistent with bimolecular substitution theory.[2] In acac$Rh(C_2H_4)_2$, Rh has the electronic structure [Kr] $5s^24d^{10}5p^4$ which is two electrons short of rare gas configuration. With a small increase in energy, Rh(I) can accommodate two electrons of an entering ligand (thus attaining rare gas configuration) to form a five-coordinate intermediate for an SN2 displacement. However, assuming C_5H_5 donates six electrons, Rh in π-$C_5H_5Rh(C_2H_4)_2$ is [Kr] $5s^24d^{10}5p^6$, and an SN2 reaction is inhibited because the electrons of the entering nucleophile would have to be promoted into a high-energy orbital.

Ethylene in π-$C_5H_5Rh(C_2H_4)_2$ is readily displaced in a bimolecular reaction by electrophiles. The Rh atom can be considered to have an unshared pair of d^2sp^3 electrons and thus add a Lewis acid to form the requisite intermediate.[4]

The inertness of π-$C_5H_5Rh(C_2H_4)_2$ to SN2 attack by nucleophiles provides the opportunity for study of ligand displacement by a third mechanism, *viz.*, dissociation of an ethylene ligand (eq 1 and 2). We have

$$\pi\text{-}C_5H_5Rh(C_2H_4)_2 \longrightarrow \pi\text{-}C_5H_5Rh(C_2H_4) + C_2H_4 \qquad (1)$$

$$\pi\text{-}C_5H_5Rh(C_2H_4) + L \longrightarrow \pi\text{-}C_5H_5Rh(C_2H_4)L \qquad (2)$$

found that this mechanism becomes available above about 115°, and by studying the kinetics of reaction 1 in the gas phase we have tentatively evaluated the strength of the rhodium–ethylene bond in π-$C_5H_5Rh(C_2H_4)_2$.

Dissociative Displacement in Solution

Displacement of ethylene from π-$C_5H_5Rh(C_2H_4)_2$ by a nucleophile was demonstrated by heating a solution of 0.070 mmol of π-$C_5H_5Rh(C_2H_4)_2$ and 1.0 mmol of 1,5-cyclooctadiene in 5 ml of diphenyl ether at 136°. Ethylene was evolved (0.126 mmol after 1 hr) and after 1.5 hr π-C_5H_5Rh(1,5-COD) was recovered (>90% conversion).

In order to substantiate the mechanism of this reaction we studied the kinetics of ethylene displacement from π-$C_5H_5Rh(C_2H_4)_2$ by various ligands. If the

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